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TRANSFORMATION IN GLASS FORMING
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Kinetics of Phase Transformation in Glass Forming Systems

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Task Objectives

Traditional experimental methods for determining the kinetic parameters essential for predicting phase formation and microstructural evolution are laborious and time consuming, particularly for the evaluation of the nucleation rates. Nonisothermal calorimetric studies, sampling phase transformations kinetics over a range of temperatures in one measurement, can be easily made in short times and require only small quantities of sample. Also, automation of nonisothermal data collection should be easier, allowing such measurements to be made at remote locations, such as in a microgravity environment. These techniques, however, suffer from the lack of quantitative methods for analysis. Existing methods are based on erroneous assumptions for the temperature dependence of the effective rate constants, generally resulting in misinformation about the transformations.

The objectives of this research were to develop realistic computer models for realistic simulations of first-order phase transformations, in particular crystallization of liquids and glasses, and to design experiments to test those models. For this study, glasses transforming to crystals of the same composition were taken. The predicted outcome of this research was improved methods for the analysis of kinetic studies of such transformations, allowing, for example, kinetic parameters for nucleation and growth to be determined from peak profile studies of differential scanning calorimetry (DSC) and differential thermal analysis (DTA) data.

Task Description

Computer programs were written to model crystallization of glasses that devitrify polymorphically by homogeneous and heterogeneous nucleation. No *ad-hoc* assumptions concerning the nucleation rate or growth velocities were made. Glass formation and DSC nonisothermal scans were simulated by computing the rate of volume fraction transformed under nonisothermal conditions by dividing the time into a series of isothermal scans of size δT and duration $\delta t = \delta T/Q$, where Q is the scan rate in degrees per second. The nucleation rate, $I(n,t)$, is evolved in each interval following the dynamical equations underlying the classical theory of nucleation. At the end of the interval, the sizes of nuclei generated in previous intervals were calculated using the cluster size-dependent growth rate, $u(r)$. The extended volume fraction transformed, x_e , is calculated at the end of each interval using the Johnson-Mehl-Avrami (JMA) formalism to take statistical account of overlapping crystallites. Since experimental measurements showed that surface crystallization was important in these transformations, new methods were developed to incorporate this. Further, since many DSC and DTA data are taken from samples consisting of fine particles of glass, methods for taking proper account of finite size effects were developed and incorporated. A modification of the JMA equation was

developed to take these effects into account; this was tested with a lattice computer calculation.

The crystallization of silicate based glasses was studied by DTA and DSC; experimental results were compared with computer model predictions. Lithium disilicate glass ($\text{Li}_2\text{O}\cdot\text{SiO}_2$) was used for most calculations and experimental measurements since the necessary kinetic and thermodynamic parameters were best known in that system. Other glasses studied included soda-lime silicate ($\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 3\text{SiO}_2$) and barium disilicate ($\text{BaO}\cdot 2\text{SiO}_2$). Changes in peak profile parameters, peak height, peak location and peak width were studied as a function of scan rate, preannealing treatments, amount of heterogeneous nucleating agents and particle size. Direct measurements of the heterogeneous nucleation rate and transient time were made to provide input materials parameters.

The computer modeling of glasses, some of the DTA studies, and all of the nucleation rate measurements was carried out at Washington University,. The glasses were prepared and most of the experimental calorimetric measurements out by Dr. Chandra Ray at the University of Missouri, Rolla, MO, working under a coordinated NASA grant.

Task Significance

The computer models developed describing nucleation and growth under isothermal and nonisothermal conditions by simulating directly the evolution of the non-equilibrium cluster distributions will have wide applicability for phase transformation studies. In particular, they will allow real-time experimental studies of phase stability and transformation in a microgravity environment.

Research Results

Our approach was shown to be valid, demonstrating good agreement between experimental and theoretical data. Commonly used methods of analysis were shown to be invalid. New analytical methods were developed to analyze DSC data and to replace the Johnson-Mehl-Avrami analysis in systems where finite particle size are expected to be important. Significant results of this research include:

1. First predictions of novel behavior of the nucleation rate during a nonisothermal DSC scan.
During the scan, the temperature dependent transient nucleation rate, $I(T)$, initially increases beyond the steady state rate, $I^s(T)$, with the magnitude of the overshoot and the peak of $I(T)$ increasing with increasing DSC scan rate. Our calculation shows that this behavior originates in the cluster evolution. Though not yet observed experimentally, similar behavior has been found, both experimentally and theoretically, for isothermal nucleation rate measurements on glasses that have undergone preannealing treatments at various temperatures. These effects demonstrate that all existing methods for predicting transient nucleation behavior, relying on a single relaxation time, are at some level flawed. The types of shape changes in the cluster distribution observed here cannot be described in terms of a single relaxation time.
2. Assessment of suggested method for using DSC curves to estimate nucleation behavior.
Based on an experimental study of lithium disilicate glass, C. Ray and D. Day (J. Am. Ceram. Soc., 73, 439 (1990)), suggested that the temperature of the maximum nucleation rate could be determined by first heating the glass isothermally in the DSC or DTA at a sufficiently low temperature to promote crystal nucleation, and subsequently measuring the temperature of the maximum rate of transformation, T_p and the peak height at T_p , upon nonisothermal heating.

The minimum in a plot of T_p (or maximum in the peak height) vs the annealing temperature should correspond to the maximum in the nucleation rate. Using the parameters for nucleation in lithium disilicate, our model predictions for the DSC peak heights (scan rate of 15°C/min) as a function of the preannealing temperature (assuming 3 hour preanneals) compared favorably with experimental data. A maximum in the DSC peak height peak is observed near the peak in the steady state rate, though they not coincide exactly. A minimum in the peak temperatures and peak widths is also observed. Similar calculations for $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ glass, however, show that the proposed correlation is not universal; it depends significantly on the degree of overlap between the zones of nucleation and growth for the glass.

3. Assessment of Kissinger method for analyzing nonisothermal data.

Using the parameters for lithium disilicate, DSC curves were calculated as a function of scan rate for a glass quenched at 1°C/s. As expected, a Kissinger plot of the simulated data (plot of $\ln[(Q/T_p^2)]$ vs. $1/T_p$) yields a straight line with slope corresponding to an activation energy of 1.77 eV. The activation energy of the effective kinetic constant, computed directly from the input parameters for nucleation and growth used, however, varies between 6.8 eV and 1.3 eV over the range of peak temperatures observed. The Kissinger value is close to that activation energy for growth alone. These results indicate that interpretations based on the Kissinger analysis should be made with caution. They will be reasonably sound for transformations based on growth alone, but should be viewed with caution for transformations involving both nucleation and growth.

4. Simulations of DSC peaks made after samples were scanned at different rates through the nucleation zone

We used the calculations to calculate the shift in peak profile parameters for glasses that had been scanned at different rates through the temperature region for significant nucleation. Though similar to the experiments described in (1), this provided another set of experiments against which we could test our model predictions. Good agreement with experimental data was found only when surface and finite size corrections were taken into account.

5. Simulations of DSC peaks made on samples as a function of Pt content

To investigate possible effects of nucleating agents, glasses were prepared with different concentrations of Pt to act as heterogeneous sites. Nucleation rates were measured directly and shown to be in good agreement with predictions based on the spherical cap model. The first quantitative transient times for nucleation were also measured and found to be in excellent agreement with a theory developed earlier by us (A. L. Greer, P. V. Evans, R. G. Hamerton, D. K. Shangguan and K. F. Kelton, *J. Cryst. Growth*, **99**, 38 (1990)). Using these data, shifts in the DSC peak profile parameters were computed for different numbers of heterogeneous sites. These agreed well with experimental data taken by us.

6. Particle size effects and surface nucleation and growth

While DSC samples are typically in the form of small powders, little account has been taken of the possible effects of finite size and surface nucleation, which we have found to be appreciable in the lithium disilicate samples that we have studied. A simple method, suggested by us, was incorporated into the calculations; the average extended volume, x_e , that exceeded the particle dimensions was computed and subtracted from the total transformed volume. This was shown to be valid when the number of growing clusters per particle exceeded about 10. Our analytical expression was extended to smaller clusters following insight gained by studying the growth of particles in a lattice using Ising-type considerations. Incorporating this

into the simulation and taking account of the surface growth, we demonstrated excellent agreement between predicted and experimentally measured DSC peak profiles, made on particles of different size. This is the first time that corrections to the standard JMA equation have been obtained for these conditions and the first time that they have been taken into account for the analysis of DSC data.

Summary of research results

In summary, we have developed computer models to simulate isothermal and nonisothermal calorimetric data. These can be used to guide the development of new methods of analysis of DSC and DTA data and to test proposed correlations. Proper account is taken of time-dependent nucleation, cluster-size dependent growth, surface nucleation and finite particle size effects. The computed trends agree well with experimental data. The sensitivity of a quantitative comparison between the calculated and experimental results is encouraging, since it suggests that it should be possible to refine our knowledge of kinetic and thermodynamic parameters by fitting to experimental calorimetric data.

Papers and presentations on work supported by this contract

Several papers have been written discussing this work. Several more are currently being written or are planned. The research is completed for these manuscripts; they should be finished within the next few months.

Manuscripts in print and in press

1. "Estimation of the Nucleation Rate by Differential Scanning Calorimetry,"
K. F. Kelton, J. Am. Ceram. Soc., **75**, 2449-52 (1992).
2. "Transient Nucleation in Glasses,"
K. F. Kelton, in *Ceramic Transactions, Nucleation and Crystallization in Liquids and Glasses*, (M. C. Weinberg, ed.), the American Ceramic Society, 45-54 (1993).
3. "Numerical Model for Isothermal and Non-Isothermal Crystallization of Liquids and Glasses"
K. F. Kelton, J. Non-Cryst. Solids, **163**, 283-296 (1993).
4. "Calculation of Macroscopic Growth Rates from Nucleation Data,"
K. F. Kelton and M. C. Weinberg, J. Non-Cryst. Solids (in press).
5. "Transient Nucleation in Glasses,"
K. F. Kelton, Mat. Sci. and Eng. (in press).

Manuscripts under preparation

1. "Heterogeneous Nucleation and Crystallization in $\text{Li}_2\text{O}\cdot\text{SiO}_2$ Glass - Experimental Measurements and Computer Modeling,"
K. L. Narayan, K. F. Kelton and C. S. Ray
(to be submitted to J. Non-Cryst. Solids)

2. "Nonisothermal Calorimetric Measurements as a Function of Size and Preannealing Treatment, I: Experimental Measurements,"
W. Huang, K. L. Narayan, T. Cull, C. S. Ray and K. F. Kelton
(to be submitted to J. Non-Cryst. Solids)
3. "Nonisothermal Calorimetric Measurements as a Function of Size and Preannealing Treatment, I: Experimental Measurements,"
K. F. Kelton, K. L. Narayan, T. Cull, W. Huang, and C. S. Ray
(to be submitted to J. Non-Cryst. Solids)
4. "Assessment of the Validity of Methods for Analyzing Nonisothermal Phases Transformations"
K. F. Kelton
(to be submitted to Acta Metall.)
5. "Extension of Johnson-Mehl-Avrami Formalism to Include Finite Size Effects"
L. Levine, K. L. Narayan, K. F. Kelton
(to be submitted to Acta Metall.)

Invited Seminars

1. "Transient Nucleation in Glasses," K. F. Kelton, Fourth International Symposium on Nucleation and Crystallization in Liquids and Glasses, August 16-19, 1992, Stone Mountain, GA.
2. "Transient Nucleation in Liquids and Glasses," K. F. Kelton, Invited Seminar, NASA, August 20, 1992, Huntsville, AL.
3. "Computer Modeling of Nonisothermal Phase Transformations," K. F. Kelton, Invited Seminar, Department of Materials Science and Engineering, Harvard University, Cambridge, MA, April, 15, 1993.
4. "Modelling of Time Dependent Nucleation," K. F. Kelton, Invited Colloquium, Department of Materials Science, University of Surrey, Guildford, UK, October 12, 1993.
5. "Computer Simulations of Nucleation in Phase Transitions," K. F. Kelton, Invited Seminar, Department of Materials, Oxford University, October 21, 1993, Oxford, UK.
6. "Computer Simulations of Non-Isothermal Phase Transitions," K. F. Kelton, Invited Seminar, Department of Engineering Materials, University of Sheffield, Sheffield, UK, October 27, 1993.
7. "Computer Calculations of Transient Nucleation," K. F. Kelton, Institut für Werkstoffphysik and Strukturforschung, Universität Bremen, Bremen, Germany, November 11, 1993.
8. "Computer Simulations of Non-Isothermal Phase Transformations," K. F. Kelton, Invited Seminar, Department of Materials Science and Engineering, Cambridge University, Cambridge, UK, November 3, 1993.
9. "Time Dependent Nucleation," K. F. Kelton, Invited Seminar, Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, MD, February 16, 1994.

10. "Transient Nucleation in Glasses," K. F. Kelton, Indo-US Workshop on "Nucleation and Growth in Solids," Bangalore, India, March, 1994.
11. "Computer Calculations of Nonisothermal Crystallization," K. F. Kelton, American Ceramics Society Meeting, Indianapolis, IN, April, 1994.

Conference Presentations

1. "Computer Simulations of Time Dependent Nucleation and Growth," K. F. Kelton, March American Physical Society Meeting, Indianapolis, IN, March 1992.
2. "Computer Simulations of Nucleation and Growth in Silicate Glasses," K. F. Kelton, American Ceramic Society Meeting, Minneapolis, MN, April, 1992.
3. "Critique of Existing Techniques for Analysis of Nonisothermal Kinetic Studies," American Physical Society Meeting, Seattle, WA, March, 1993.
4. "Macroscopic Crystal Growth Rates and Classical Nucleation Theory," K. F. Kelton and M. C. Weinberg, American Ceramics Society Meeting, Indianapolis, IN, April, 1994.
5. "Heterogeneous Nucleation in Lithium Disilicate Glass," K. L. Narayan, T. C. Cull, K. F. Kelton, American Ceramics Society Meeting, Indianapolis, IN, April, 1994.
6. "Computer Model for Non-Isothermal Crystallization," K. Lakshmi Narayan, L. E. Levine, K. F. Kelton and T. S. Cull, Midwest Solid State Conference, Kansas City, MO, October, 1994.
7. "Finite Size Corrections to the Johnson-Mehl-Avrami Equation," L. E. Levine, K. Lakshmi Narayan, and K. F. Kelton, Midwest Solid State Conference, Kansas City, MO, October, 1994.

Future work

These investigations have been very successful, demonstrating the validity of our basic approach. We have developed computer models that describe crystallization in a model system involving time-dependent homogeneous and heterogeneous nucleation, cluster-size-dependent growth, finite particle size effects, and surface growth. We have identified key parameters from DSC and DTA data that lend themselves to analysis, peak location, peak width and peak height. To develop this into a general purpose program, useful for a general analysis of calorimetric data, however, much more work is required. Important points include:

1. The extension of this modeling to other glass systems. Preliminary work done on two glasses, soda-lime silicate ($\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$) and barium disilicate ($\text{BaO} \cdot 2\text{SiO}_2$), suggest that our modeling approach is valid there also. This should be checked more extensively.

2. The model must be extended to include systems that devitrify by a primary mechanism, involving a compositional difference between the parent and daughter phases. A coherent program will require both experimental and theoretical investigations of a more basic nature than were conducted under this grant. We are currently beginning this. Preliminary computer programs written by us show that the evolution of the clusters is going to be substantially more complicated. The cluster composition is not constant, changing with cluster size.
3. The effects of heterogeneous nucleation should be investigated further. For the Pt, the contact angle was high, $\approx 120^\circ$. The experimental data verified our earlier predictions, however, in a region where little change in the transient time was expected. Nucleating agents have smaller contact angles would allow a better test of our model predictions and would allow a broader exploration of the effects of heterogeneous nucleation on DSC and DTA peak profiles